Statistical and Thermal Physics: Homework 5

Due: 7 February 2020

1 Differentiation of multivariable functions

Consider an ideal gas and suppose that a function of interest satisfies

$$F = PV^n$$

where n is an integer.

a) Determine $\left(\frac{\partial F}{\partial T}\right)_V$ and $\left(\frac{\partial F}{\partial T}\right)_P$. Eliminate T to rewrite the results in terms of P and V.

b) Determine values of n for which $\left(\frac{\partial F}{\partial T}\right)_V = \left(\frac{\partial F}{\partial T}\right)_P$.

2 Differentiation identities

Consider three variables x, y, z that are not independent. This means that they are related by some function, which could be written $z = z(x, y)$ or $y = y(x, z)$ or $x = x(y, z)$ depending on the choice of independent variables. These functions can all be differentiated with respect to their variables; the derivatives must be related. This exercise will result in general relationships between these derivatives that are always satisfied.

a) To illustrated this let $z = x^2y$. So $z(x, y) = x^2y$. Find expressions for $x = x(y, z)$ and $y = y(x, z)$. Determine expressions for

$$\left(\frac{\partial z}{\partial y}\right)_x, \quad \left(\frac{\partial z}{\partial x}\right)_y, \quad \left(\frac{\partial x}{\partial y}\right)_z, \quad \left(\frac{\partial x}{\partial z}\right)_y, \quad \left(\frac{\partial y}{\partial x}\right)_z, \text{and} \quad \left(\frac{\partial y}{\partial z}\right)_x.$$

According to your results how are $\left(\frac{\partial z}{\partial y}\right)_x$ and $\left(\frac{\partial y}{\partial z}\right)_x$ related to each other? How about $\left(\frac{\partial z}{\partial x}\right)_y$ and $\left(\frac{\partial x}{\partial z}\right)_y$?

b) To prove these relationships *for any function*, first consider x and y as the independent variables. Express $\mathrm{d}z$ in terms of $\mathrm{d}x$ and $\mathrm{d}y$, using appropriate partial derivatives. Note that this must be done for any function $z(x, y)$, not just the special case above. Then express $\mathrm{d}x$ in terms of $\mathrm{d}y$ and $\mathrm{d}z$, using appropriate partial derivatives. Substitute this into the general expression for $\mathrm{d}z$; this will give an expression for $\mathrm{d}z$ in terms of $\mathrm{d}x$ and $\mathrm{d}z$. Use the expression to show that

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = 1 \quad \text{and} \tag{1}$$

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x. \tag{2}$$

These identities will be important throughout the subject.

c) Check that the identities are valid for the function $z(x, y) = x^2y$.

d) There is nothing special about the order of the variables in Eqs. (1) and (2). You could permute the variables as $x \to y, y \to z$ and $z \to x$ and the identities must still be valid. Do this and check the resulting identities for $z = x^2y$.

e) Check these identities for an ideal gas, with $z \to P, x \to T$ and $y \to V$.

3 Heat capacities for an ideal gas

Consider monoatomic gases. For an ideal gas,

$$E = \frac{3}{2}NkT.$$

a) Using the energy, E, determine c_V and c_P for this gas.

b) Explain, in terms of the energy involved in the processes to measure the two heat capacities, why you would expect $c_P > c_V$.

a) $F = PV^n \implies F = F(P,V) = PV^n$

Then we need this in terms of T, V. Here $P = NkT/V$

$$\implies F = \frac{NkT}{V} V^n \implies \boxed{F = F(T,V) = NkTV^{n-1}}$$

So

$$\boxed{\left(\frac{\partial F}{\partial T}\right)_V = NkV^{n-1}}$$

Now for $\left(\frac{\partial F}{\partial T}\right)_P$ we need $F = F(P,T)$ and so with $V = \frac{NkT}{P}$

$$F = P\left(\frac{NkT}{P}\right)^n \implies \boxed{F = (Nk)^n T^n P^{1-n}}$$

Then

$$\left(\frac{\partial F}{\partial T}\right)_P = n T^{n-1} (Nk)^n P^{1-n}$$

and $T = \frac{PV}{Nk} \implies \left(\frac{\partial F}{\partial T}\right)_P = n \frac{\cancel{P^{n-1}} V^{n-1}}{(Nk)^{n-1}} (Nk)^n \cancel{P^{1-n}}$

$$\implies \boxed{\left(\frac{\partial F}{\partial T}\right)_P = nNkV^{n-1}}$$

b) This requires

$$\left(\frac{\partial F}{\partial T}\right)_V = \left(\frac{\partial F}{\partial T}\right)_P \iff \cancel{NkV^{n-1}} = n\cancel{NkV^{n-1}}$$

$$\iff \boxed{1 = n}$$

It requires $\boxed{n=1}$.

a) $z = x^2 y \qquad x = \sqrt{\frac{z}{y}} \qquad y = \frac{z}{x^2}$

$$\left(\frac{\partial z}{\partial y}\right)_x = x^2 \qquad \left(\frac{\partial x}{\partial y}\right)_z = -\frac{1}{2}\sqrt{z}\, y^{-3/2} \qquad \left(\frac{\partial y}{\partial z}\right)_x = \frac{1}{x^2}$$

$$\left(\frac{\partial z}{\partial x}\right)_y = 2xy \qquad \left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{2} z^{-1/2} y^{-1/2} \qquad \left(\frac{\partial y}{\partial x}\right)_z = -\frac{2z}{x^3}$$

$$\left(\frac{\partial z}{\partial y}\right)_x = x^2 \quad \left(\frac{\partial y}{\partial z}\right)_x = \frac{1}{x^2} \Rightarrow \boxed{\left(\frac{\partial z}{\partial y}\right)_x = 1\Big/\left(\frac{\partial y}{\partial z}\right)_x}$$

$$\left(\frac{\partial z}{\partial x}\right)_y = 2xy \quad \left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{2}\frac{1}{\sqrt{yz}} = \frac{1}{2}\frac{1}{\sqrt{x^2y^2}} = \frac{1}{2xy} \Rightarrow \left(\frac{\partial z}{\partial x}\right)_y = 1\Big/\left(\frac{\partial x}{\partial z}\right)_y$$

b) $$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$dx = \left(\frac{\partial x}{\partial z}\right)_y dz + \left(\frac{\partial x}{\partial y}\right)_z dy$$

$$\Rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y \left[\left(\frac{\partial x}{\partial z}\right)_y dz + \left(\frac{\partial x}{\partial y}\right)_z dy\right] + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\Rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y dz + \left[\left(\frac{\partial z}{\partial y}\right)_x + \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z\right] dx$$

$$\Rightarrow 0 = \left[\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y - 1\right] dz + \left[\qquad\qquad\right] dx$$

This is only possible for all dx, dz if

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = 1 \qquad \text{AND} \qquad \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x$$

c) Using results from a)

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = \cancel{2}xy \, \cancel{\tfrac{1}{2}} \frac{1}{\sqrt{zy}} = \frac{xy}{\sqrt{x^2y^2}} = 1$$ ✓

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = 2xy\left(-\tfrac{1}{2}\sqrt{z}\; y^{-3/2}\right)$$

$$= -\, x y^{-1/2} z^{1/2}$$

$$= -\, x\sqrt{\frac{z}{y}} = \underbrace{-x^2}_{\left(\frac{\partial z}{\partial y}\right)_x}$$ ✓

d) Check $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = -\frac{1}{2}\overbrace{\sqrt{\frac{z}{y}}}^{x}\,\frac{1}{y}\left(-2\frac{z}{x^3}\right)$

$$= \frac{x}{y}\,\frac{z}{x^3} = \frac{x\,x^2y}{y\,x^3} = 1$$

So $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$ ✓

Check $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$

$$-\frac{1}{2}\sqrt{\frac{z}{y}}\,\frac{1}{y}\,\frac{1}{x^2}$$

$$= -\frac{1}{2}\sqrt{\frac{x^2\cancel{y}}{\cancel{y}}}\,\frac{1}{y}\,\frac{1}{x^2} \qquad -\frac{1}{2}\frac{1}{\sqrt{yz}} = -\frac{1}{2}\frac{1}{\sqrt{x^2y^2}}$$

$$= -\frac{1}{2}\frac{1}{yx} \qquad = -\frac{1}{2}\frac{1}{xy}$$

agree ✓

e) Need to check:

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V = 1 \qquad \text{AND} \qquad \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P = -\left(\frac{\partial P}{\partial V}\right)_T$$

$$P = \frac{NkT}{V} \quad \Rightarrow \quad T = \frac{PV}{Nk}$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V} \quad \Rightarrow \quad \frac{\partial T}{\partial P} = \frac{V}{Nk}$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V = \frac{Nk}{V}\frac{V}{Nk} = 1$$

works!

$$\underbrace{\frac{Nk}{V} \quad \frac{P}{Nk}}_{= \frac{P}{V}} \qquad \underbrace{-\left(-\frac{NkT}{V^2}\right)}_{= \frac{PV}{V^2} = \frac{P}{V}}$$

works!

a) $C_v = \left(\frac{\partial E}{\partial V}\right)_T$

and $E = E(V,T) = \frac{3}{2}NkT$

$\Rightarrow \left(\frac{\partial E}{\partial V}\right)_T = \frac{3}{2}Nk \Rightarrow C_v = \frac{3}{2}Nk$

Now $C_p = \left(\frac{\partial E}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p$

and $E = E(P,T) = \frac{3}{2}NkT$

$\Rightarrow \left(\frac{\partial E}{\partial T}\right)_p = \frac{3}{2}Nk.$

Also $V = NkT/p \Rightarrow \left(\frac{\partial V}{\partial T}\right)_p = \frac{Nk}{p}$

$\Rightarrow P\left(\frac{\partial V}{\partial T}\right)_p = Nk$

Thus $C_p = \frac{3}{2}Nk + Nk \Rightarrow C_p = \frac{5}{2}Nk$

b) $dE = \delta Q - PdV \Rightarrow \delta Q = dE + PdV$ $\qquad C_v = \frac{\delta Q}{dT}$

At constant volume all heat goes to changing E

At constant pressure some heat goes into work done by the gas. So a smaller portion of heat is devoted to changing E

The change in E is proportional to change in T

So at constant volume change in T is greater ~~per~~ heat change $\Rightarrow C_v$ smaller.